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Recycling a Carbon Fibre Reinforced Polymer with a Supercritical Acetone/Water Solvent Mixture: Comprehensive Analysis of Reaction Kinetics

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Abstract

The decomposition of a carbon fibre reinforced epoxy resin with an acetone/water solvent supplied in the ratio of 80:20 v/v has been investigated using a non-stirred batch reactor. Temperatures and pressures in the range of 300 to 380°C and 16 to 30 MPa were studied over a reaction time of up to 150 min using an initial reactor loading of 30 g_{resin} $L_{solvent}^{-1}$. The minimum conditions necessary for effective fibre recovery were identified as 320°C and 20 MPa. After processing for 120 min at this temperature and pressure, up to 95 wt.% of the resin was stripped from the fibre surface and the original weave architecture was retained. Increasing the reactor loading to 90 g_{resin} $L_{solvent}^{-1}$ demonstrates no significant effect on the extent of resin decomposition. This, combined with imaging using X-ray computer tomography, suggests that the solvent is always in excess and that the mass transfer of the solvent into the composite and degradation products away from the surface is fast. A first order reaction rate equation based on the Arrhenius expression and a reaction-rate limited shrinking core model (SCM) have both been successfully fitted to the experimental data. From this, the parameters activation energy and frequency factor have been calculated to be 222.3 kJ mol^{-1} and 7.64 $x10^{17}$ min^{-1} respectively for the Arrhenius model and 164.3 kJ mol^{-1} and 1.29 $x10^{12}$ min^{-1} for the SCM. The results presented in this work demonstrate that either approach can be used to predict the resin decomposition to within ± 5% which is similar to the margin of experimental error.

Keywords: Recycling, Composites, Carbon fibres, Thermosetting resin, Solvolysis

1 Introduction

Due to their high strength, low density and excellent resistance to corrosion and fatigue, carbon fibre reinforced polymers (CFRPs) are becoming more frequently used across the aeronautics, automotive and energy industries, resulting in an expected increase in global production to 194,000 t by 2022 [1]. However, there is a large energy demand associated with the manufacture of virgin carbon fibres (vCF, 198 – 595 MJ kg^{-1} [2]) and epoxy resins (76 – 80 MJ kg^{-1} [3]). Recycling 1 kg of waste CFRP via chemical methods requires an estimated 38.4 MJ kg^{-1} [2]; assuming a fibre content of 65 wt.%, this represents a reduction in energy demand of 78 – 91% when compared to virgin material. Previous work has also demonstrated that there is up to an 85% financial saving in utilising fibres recovered from a fluidised bed process, rather than vCF [4]. It is therefore economically and environmentally beneficial to recycle both manufacturing and end-of-life CFRP waste. Currently commercialised techniques focus on pyrolysis which is able to regenerate good quality fibres retaining 90% of their tensile strength compared to vCF [5]. However, this is a resource inefficient process due to the loss of the resinous matrix which typically makes up 30-50 wt.% of the composite material [6]. In order to close the loop of the supply chain, chemical recycling methods have started to gain more attention.

For solvent systems operating under low temperature and pressure (LTP - ≤ 200°C, 100 kPa), it is necessary to use strong, highly concentrated, acidic or basic catalysts in order to achieve sufficient degradation of the matrix. Although less extreme conditions provide better reaction control, these media may cause significant fibre damage, limiting their use in future applications [5-7]. The inclusion of hydrogen peroxide in acidic systems facilitates the recovery of high quality material, however, there are typically longer processing times and the production of hazardous wastes which are harmful in terms of human health, safety and the environment [8-10]. For these reasons, this work focuses on the development and analysis of a high temperature and pressure (HTP) system which avoids the use of catalysts and strong acids.

By operating at near- or supercritical conditions, fluids exhibit enhanced diffusivity, better mass transport and a density dependant solvating power [7]. Sub- and supercritical water [8, 9], short-chain alcohols [14-17] and acetone [10, 11] have been investigated and all are able to fully separate the fibres from the resin when operating under batch conditions at temperatures ranging from 320 to 450°C. When less severe conditions are used, fibre integrity is also maintained [14, 16, 19]. It has been suggested that the preferred reaction mechanism for the degradation of epoxy resins is hydrolysis [3]. Following this, there has been some investigation into the effect of mixing water with generally recognised as safe (GRAS) solvents [12, 3, 13]. Using a model epoxy, a process temperature of 350°C and a reaction time of 30 min, Oliveux, et al. (2015) demonstrated that a mixture

of acetone and water, supplied at a ratio of 80:20 v/v, was able to achieve the most effective degradation when compared with other GRAS solvent/water mixtures [3]. This solvent system has also been used to recycle a commercial CFRP and demonstrated the recovery of high quality fibres [13], however, understanding of the degradation process and reaction kinetics remains limited. Although previous studies have applied Arrhenius-type rate equations [13, 18] or a shrinking core model (SCM) [11] to the decomposition of a thermoset resin, only a small number of temperatures have been considered. The research presented, therefore, aims to identify the rate determining steps within the degradation process, to develop a kinetic expression based on the Arrhenius equation and to apply an SCM to further characterise the developed technique. This is a comprehensive investigation where both approaches have been considered simultaneously for the first time whilst studying a larger number of conditions [9, 10, 11]. As part of this work, optimum operating parameters with regards to the process temperature, pressure, reaction time and reactor loading are also identified.

2 Materials & Methods

2.1 Materials

The composite material investigated was supplied by a leading aerospace manufacturer and consisted of a commercial RTM6 thermoset epoxy resin reinforced with 20 plies of Toray T700 6k carbon fibre woven fabric. From this, samples were cut into pieces measuring (10 x 10 ± 1) mm^2 and the thickness was 6 ± 0.1 mm. The manufacturer's data quotes a fibre volume content of 53 ± 1 vol.% which is equivalent to a resin content of 36 wt.% using densities of carbon fibre and resin of 1.80 and 1.15 kg m^{-3} respectively [14, 15]. The resin content was also determined by thermogravimetric analysis (TGA) using a Seiko Intstruments Ltd. Exstar 6000 and was calculated to be 35 wt.%. Due to commercial sensitivity, the exact formulation, and therefore density of the resin, is not known and for this reason the value of 35 wt.% is used in all subsequent calculations. The material was further characterised by differential scanning calorimetry (DSC) using a Mettler Toledo DSC 1 Star System. The glass transition temperature (T_g) was identified between 210 and 230°C thus indicating a high degree of cross-linking above 0.9 [16]. Currently, 72% of CFRPs manufactured use thermoset resins as the matrix material [1] and are amongst the most difficult to decompose [17]. Therefore, if it is possible to fully separate the fibres from this RTM6 resin, the developed process is likely to be suitable for recycling a wide range of CFRPs.

Analytic research grade acetone was purchased from Sigma Aldrich and was used as delivered. This was mixed with water in the ratio of 80:20 v/v which corresponds to a mole fraction of acetone of 0.495. Distilled water with a conductivity of 0.05 mS cm^{-1} was produced on site, however, water from the mains supply (conductivity = 0.16 mS cm^{-1}) was also used in some experiments in order to more closely simulate industrial conditions. The pH of the mains water was recorded as being 7.8 ± 0.3 and the expected composition is provided in Table 1 [18].

Substance	**Concentration (mg L^{-1})**		
	Minimum	**Average**	**Maximum**
Aluminium	0.005	0.009	0.014
Ammonium	0.012	0.014	0.018
Boron	0.012	0.014	0.018
Bromate	0.00083	0.00131	0.00169
Chloride	12.79	15.15	18.63
Chlorine	0.15	0.42	0.72
Copper	0.0020	0.0150	0.0364
Cyanide	< 0.001	< 0.002	< 0.002
Fluoride	0.57	0.72	0.82
Iron	0.01	0.02	0.192
Manganese	0.0003	0.0012	0.0096
Nickel	0.0011	0.0014	0.0022
Nitrate	2.26	3.39	4.75
Sodium	9.7	11.2	13.0
Sulphate	16	22	28
Total organic carbon (TOC)	0.8	1.0	1.4
Total Trihalomethanes	0.01755	0.02625	0.03625

Table 1. Composition of mains supply water [18].

2.2 Fibre Recovery

All experiments were completed with 50 mL of the solvent mixture in a stainless steel, 100 mL tubular reactor. This was electrically heated to temperatures ranging from 300 to 380°C and was held at the desired temperature from 0 to 150 min as specified in Table 3. To prevent pyrolysis of the material due to contact with the reactor walls, all samples were placed in a stainless steel basket which was suspended in the solvent system. The total heating phase was 35 ± 5 min and the reactor was cooled to room temperature in 25 ± 3 min using forced air convection. Fibres were recovered and washed with acetone at ambient conditions to remove the degradation products which had adhered to the surface during the cooling phase. Samples were then dried in a fume cupboard overnight before being analysed. For the experiments detailed in Table 3, an initial reactor loading of 30 g_{resin} $L_{solvent}^{-1}$ was used. This was later increased to 60 and 90 g L^{-1} at the conditions described in Table 4 in order to examine the ability of this system to degrade larger quantities of material at similar process parameters.

Temperature (± 1°C)	Induced Pressure (± 0.3 MPa)	Reaction Times, t_r (min)
300	15.8	
310	17.8	30, 120
320	19.7	
330	22.0	30, 90
340	23.5	15, 45
360	27.0	0, 15
380	30.0	0

Table 2. Reactor conditions used for the degradation of RTM6 composite material using acetone and distilled water in the ratio 80:20 v/v.

2.3 Solvent Characterisation

As the operating conditions cover a range between the critical points of acetone (235°C, 4.8 MPa [19]) and water (374°C, 22 MPa [20]), there is some uncertainty regarding the phase of the solvent mixture. Phase equilibria calculations were performed with the Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) equation of state (EoS) as described in the literature [29-31]. This is a modern thermodynamic model

developed from statistical mechanical theories capable of handling hydrogen bonding (association) phenomena such as those present between water and acetone molecules. Equation 1 expresses PC-SAFT in terms of the addition of contributions to the residual Helmholtz free energy ($\hat{a}^{res}$).

Temperature (± 1°C)	**Induced Pressure (± 3 MPa)**	**Reaction Times, t_r (min)**
300	15.8	0, 10, 20, 30, 45, 60, 90, 120, 150
310	17.8	
320	19.7	
330	22.0	
340	23.5	
360	27.0	0, 5, 10, 15, 20, 30, 60, 90, 150
830	30.0	

Table 3. Reaction conditions used for the degradation of RTM6 composite material using acetone and mains water in the ratio 80:20 v/v.

Temperature (± 1°C)	**Pressure (± 3 MPa)**	**Reaction Time t_r (min)**
320	19.7	120
330	22.0	90
340	23.5	45
360	27.0	20

Table 4. Conditions investigated with an increased reactor loading of 60 and 90 $g_{resin}\,L_{solvent}^{-1}$ (175 and 257 $g_{composite}\,L_{solvent}^{-1}$)

$$\frac{\hat{a}^{res}}{RT} = \frac{\hat{a}^{hc}}{RT} + \frac{\hat{a}^{dis}}{RT} + \frac{\hat{a}^{assoc}}{RT} \quad (1)$$

Where $\hat{a}$ = Helmholtz free energy (J), R = Ideal gas constant (8.314 J mol^{-1} °C^{-1}), T = Temperature (°C) and superscripts *hc*, *dis* and *assoc* are the contributions due to hard-chain fluid formation, dispersive and associative

interactions respectively. Details for the expressions of the different contributions are described by Gross, et al. [21, 22]. Pure component parameters for the PC-SAFT model are provided in Table 5. The values for water are available in the literature [23] while the values for acetone were obtained by fitting experimental saturated pressures and liquid densities following the methodology described by Román-Ramírez, et al. [23]. A single temperature-independent binary interaction parameter (k_{ij}) for the mixture was found following a similar procedure to that described elsewhere [23]. The experimental data was taken from Othmer, et al. [24] which covers a wide range of pressures and temperatures (1 to 34.5 MPa and 57 to 230°C, respectively). The optimum value of the parameter was k_{ij} = 0.015. Deviations in T were found to be less than 0.65% for isobaric calculations at 34.5 MPa. The phase envelope for a mole fraction of acetone of 0.495 (80 vol.%) is presented in **Error! Reference source not found.**. The critical point for this solvent composition was calculated to be at 297°C and 12 MPa. The observed pressure is consistently 2.5 MPa above that calculated due to the presence of air in the reactor.

Parameter	Acetone	Water
m	2.6096	2.7028
σ (Å)	3.3366	2.0526
ε/k (K)	262.13	218.96
κ^{AB}	-	0.56142
k (J K^{-1})	-	2.045

Table 5. Pure component parameters used in PC-SAFT equation of state.

2.4 Material Characterisation

2.4.1 Resin Decomposition

The resin decomposition (RD, wt.%) was determined by two independent methods. The first considered the difference in mass before and after processing samples (m_i and m_p, respectively) at each of the conditions described in Table 2 to 4. Values obtained were then used in Equation (2).

$$RD = \frac{m_i - m_p}{R_i m_i} \times 100 \quad (2)$$

Where m_i = Initial mass of composite (g), m_p = Mass of composite after processing and R_i = Initial resin content (35 wt.%). As Equation (2) assumes that all mass loss is due to solubilisation of the polymer matrix, the second method involved calcining all solid material recovered from each experiment in air at 500°C. Samples were divided into five aluminium crucibles, heated and removed from the furnace at regular intervals. Each sample was allowed to cool to room temperature before being weighed. When the reduction in mass was negligible, it was assumed all organic material had been removed. Equation (3) was used to calculate the resin content after processing, R_P, and the RD was quantified by Equation (4). An average was then calculated from the five samples.

$$R_p = \frac{m_p - m_f}{m_p} \times 100 \quad (3)$$

$$RD = \frac{R_i - R_p}{R_i} \times 100 \quad (4)$$

Where R_p = Resin content after processing (wt.%) and m_f = Final mass of sample after calcination (g). An average value for RD was taken between the two methods described and used in all subsequent calculations.

2.4.2 X-Ray Computer Tomography (XRCT)

To study the mass transfer of the solvent molecules through the composite, a partially degraded sample was imaged with X-Ray Computer Tomography (XRCT) using a Bruker Skyscan 1172. After processing for 10 min at 320°C, a sample of composite material was mounted on to a platform and loaded into the imaging chamber. An acceleration voltage of 25 kV and current of 35 µA were used. The resolution was 240 px.mm^{-1} and the camera exposure time was set to 4 s.

3 Results and Discussion

3.1 Fibre Recovery

The effect of changing operating temperature and reaction time on the RD is presented in **Error! Reference source not found.** and 3 with the error bars showing the minimum and maximum values as

calculated by the two methods described in Section 2.4.1. Although Figure 2 demonstrates that the degradation reaction does start at some temperature below 300°C, the contribution of the heating phase to the RD is relatively small below 340°C. It is also apparent that the use of mains water does not significantly affect the degradation of the resin; any difference observed when compared to distilled water is within the range of experimental error. There is, however, a significant dependence of RD on temperature. A value of just 54% is observed after processing at 300°C for 150 min, while complete degradation is achieved in just 15 min at 360°C. This strong dependence has been previously reported [9], although it is not likely to be due to the use of a supercritical mixture as the critical point is exceeded beyond 297°C. Below 320°C, the degradation reaction appears slow and it is possible that at temperatures less than this, it is not possible to fully degrade the matrix. Despite processing for 150 min at 300°C, the plies of carbon fibre fabric remained firmly adhered to each other as shown in **Error! Reference source not found.**.

Upon raising the reaction temperature to 320°C, the plies were perfectly separated and over 90% of the resin was stripped from the fibre surface after a process time of 120 min. This suggests that in order to effectively recover fibres from an RTM6 resin, there is a minimum temperature requirement of 320°C when operating under batch conditions. Complete degradation of an epoxy resin with pure acetone has also previously been achieved at 320°C after a reaction time of just 20 min [11]. However, Okajima, et al. noted a T_g of 183°C [11] which is 37 ± 10°C lower than the RTM6 epoxy investigated in this study. This is indicative of a lower degree of cross linking thereby leading to different degradation characteristics. By increasing the reaction temperature to 330°C, a similar RD was observed in a faster processing time of just 90 min. Complete degradation of the matrix was achieved at 340°C (reaction time, t_R = 45 min) and 360°C (t_R = 15 min). This is similar to previous research which has achieved complete degradation of a model epoxy resin with this solvent mixture at 350°C in 30 min [3]. As similar conditions were necessary to fully decompose the resin, the current research suggests that there is little to no effect of the fibre on the overall degradation rate of a CFRP. Additional experiments were carried out at 380°C, however, upon reaching the target temperature, the resin was fully decomposed. Although the reaction rate is much faster at higher temperatures, more extreme conditions resulted in the loss of the fibre structure; Figure 4 shows the “fluffy” quality obtained due to temperatures in excess of 340°C. As an effective commercial realignment process is yet to be developed, it is unlikely that fibres recovered after processing a CFRP at these conditions are suitable for reuse in defined architectures, however random non-woven mats may be possible if sufficient fibre densities can be attained in the product [25]. This

suggests that the lowest operating temperature capable of fully decomposing the epoxy resin will be preferred and therefore, a reaction time of 120 min at 320°C is recommended for the effective recovery of carbon fibres.

3.2 Reactor Loading

To examine the effect of reactor loading, conditions were selected based on the results in **Error! Reference source not found.** and are shown in Table 4. **Error! Reference source not found.** illustrates that upon increasing the concentration of resin in the solvent to 60 and 90 g L^{-1}, there is no discernible difference in RD within the margin of error of the experiment. These results suggest that even with the reactor filled with CFRP to give a loading of 90 g L^{-1}, the solvent is still in excess. If the solvent were becoming saturated with the organic products, the mass transfer of the solvent through the bulk fluid, penetration into the composite and transfer of the products away from the fibre surface into the solution would slow down. This in turn would lead to a slower degradation reaction and therefore a lower RD for the conditions studied. Furthermore, previous work demonstrated there was no scale effect when using a 5 L reactor and loading of up to 60 g L^{-1} [26]. This finding has an important industrial application as results suggest that it is possible to fill a reactor with waste CFRP and still achieve complete degradation at the same operating conditions. In turn, this will mean that the financial, energy and environmental cost of recycling per kg of fibre recovered will be minimised.

3.3 X-Ray Computer Tomography

A partially degraded sample was imaged with XRCT in order to further understand the mechanism of the overall degradation process. **Error! Reference source not found.**a illustrates that there is some ply separation as the solvent molecules effectively penetrate to the centre of the sample within 10 minutes of processing at 320°C. On the surface of each ply, cracks are visible and, although the fibres appear to facilitate the mass transfer of the solvent to the centre of the sample, the reaction pathways are randomly orientated and do not follow the direction of individual fibres. This suggests that the orientation of each tow doesn't affect penetration and the solvent may therefore simply move through the resin by following defects within the polymer. By removing the higher density fibres from the image, as shown in **Error! Reference source not found.**b, it is noticeable that a large volume of resin remains in the centre of the sample. It is therefore also apparent penetration of the solvent mainly occurs through the x and y directions, possibly due to lower fibre density in between the plies while the path of solvent molecules in the z direction is always tortuous. Although mass transfer of the solvent and/or products may affect the overall degradation rate, it is likely that the process is reaction rate limited as it takes 2 h

to solubilise 90% of the resin, despite the fact that the solvent quickly reaches the centre of the composite. Previous work has studied larger samples measuring (50 x 50) to (50 x 80) mm^2 and found near-complete degradation occurs in a similar time at 320°C [26]. If the mass transfer were rate-limiting, the longer reaction pathways of larger samples would lead to an increased process time in order to effectively eliminate all resin.

3.4 Analysis of Reaction Kinetics

The relationship between resin degradation and reaction time has been previously studied through the application of both an Arrhenius-type equation [9, 10] and a reaction rate limited shrinking core model (SCM) [11]. The current work considers both approaches in order to evaluate which can be used to best describe the degradation of an RTM6 composite material.

3.4.1 Arrhenius Kinetics

Reaction kinetics can be modelled by fitting the data obtained to a kinetic equation where the reaction rate, $-r_A$, is proportional to the concentration of one or more components raised to the power of the order of reaction, *n*. **Error! Reference source not found.** illustrates that increasing the concentration of resin, and therefore the concentration of degradation products dissolved in the solvent, has little effect on the decomposition. Furthermore, as the reaction proceeds and the resin solubilised, the rate appears to decrease. As the mass fraction remaining also decreases with time, it can be stated that the rate of resin decomposition is proportional to the mass fraction of resin remaining within the composite. This is defined by Equation (5) meaning that the reaction rate can be modelled with Equation (6).

$$M = \frac{m_{resin}}{m_{composite}} = 1 - RD \tag{5}$$

$$-r_A = \frac{dM}{dt} = -\,k_{A,R}\,M^n \tag{6}$$

Where m_{resin} and $m_{composite}$ are the mass of the resin and total mass of composite respectively (g) and $k_{A,R}$ is the Arrhenius rate constant during the reaction phase (min^{-1}). As *n* is currently unknown, the variables in Equation

(6) (M and reaction time, t_R (min)) were separated and integrated to give Equation (7) which is in the form $y = mx + c$. A plot of $\frac{M^{(n-1)}}{(n-1)}$ vs. t_R should then give a straight line.

$$\frac{M^{(n-1)}}{n-1} = -k_{A,R}t + c \quad (7)$$

Where c is a dimensionless constant. Pinero, et al. have previously suggested that n=2 for supercritical water [9] and n=1.5 when using propan-1-ol [10] which takes into consideration any mass transfer effect. However, for these values, there was not a good correlation with the data obtained especially at higher temperatures; R^2 values at 360°C for n=2 and n=1.5 were 0.70 and 0.83 respectively. By manipulating the value of n, it was apparent that reducing the reaction order resulted in a closer fit between the data points and regression line. For the case n=1, integrating Equation (6) gives Equation (8) and a plot of $\ln(M)$ vs. t_R (**Error! Reference source not found.**) gives a straight line with good R^2 values in the range of 0.95 to 0.99 from 300 to 360°C thereby suggesting that the overall degradation process is first order with respect to the mass fraction of resin remaining on the surface. Values for $k_{A,R}$ were taken as the gradients of each trend line and are tabulated in Table 6.

$$\ln(M) = -k_{A,R}t + c \quad (8)$$

Temperature (°C)	$k_{A,R}$ (x10^{-3} min^{-1})	$k_{A,H}$ (x10^{-3} min^{-1})
300	4.29	0.920
310	9.33	1.41
320	19.7	4.89
330	35.0	5.75
340	108	7.91
360	333	27.2

Table 6. Arrhenius rate constants for the reaction phase ($k_{A,R}$) and heating phase ($k_{A,H}$).

For all temperatures investigated, it was observed that there was some mass loss before reaching the specified process conditions. Therefore, it is necessary to model the degradation reaction during the heating and reaction phases separately. To consider the decomposition due to the reaction phase only, Equation (6) was integrated with n=1 between the limits of M=M_T at t=t_R and M=M_H at t=0. The result is shown by Equation (9) where M_T is the total mass fraction of resin remaining after the process, M_H is the mass fraction remaining after the heating phase and t_R is the reaction time. Rearranging Equation (9) allows an expression for M_T (Equation (10)) to be obtained.

$$\ln\left(\frac{M_T}{M_H}\right) = -k_{A,R}t_R \quad (9)$$

$$M_T = M_H e^{-k_{A,R}t_R} \quad (10)$$

To solve Equation 10, an expression for M_H was found by assuming that the reaction is also first order during the heating phase. Integrating Equation (6) with k=$k_{A,H}$ where $k_{A,H}$ is the Arrhenius rate constant during the heating phase and the limits M=M_H at t=t_H and M=1 at t=0 gives Equation (11). This was rearranged to obtain Equation (12) which allowed values for $k_{A,H}$ to be found from the experimental data. These are also provided in Table 6.

$$\ln(M_H) = -k_{A,H}t_H \quad (11)$$

$$k_{A,H} = -\frac{\ln(M_H)}{t_H} \quad (12)$$

An alternative rearrangement of Equation (11) gives Equation (13) which can then be substituted into Equation (10) to model the total mass fraction of resin remaining within the composite. This is expressed by Equation (14) and the total resin decomposition is then given by Equation (15). **Error! Reference source not found.** demonstrates that the model (continuous lines) is a good fit for the individual data points at all temperatures investigated.

$$M_H = e^{-k_{A,H}t_H} \quad (13)$$

$$M_T = e^{-k_{A,H}t_H - k_{A,R}t_R} \quad (14)$$

$$RD = 1 - e^{-k_{A,H}t_H - k_{A,R}t_R} \quad (15)$$

As the rate constant is a function of temperature, the calculated values of $k_{A,H}$ can be considered an average between a theoretical initiation temperature, T_i, to the specified operating conditions. Therefore, $k_{A,H}$ can be used to calculate the value of this average temperature, T_{Av}, using a rearrangement of the linearised form of the Arrhenius expression (Equation (16)).

$$\frac{1}{T_{Av}} = \frac{1}{T_R} + \frac{R}{E_A}\ln\left(\frac{k_{A,R}}{k_{A,H}}\right) \quad (16)$$

It was assumed that T_{Av} is the midpoint between the reaction temperature and a theoretical initiation temperature T_i. If this is the case, T_i can be calculated with Equation (17).

$$T_i = 2T_{Av} - T_R \quad (17)$$

Across the temperature range 300 to 360°C, this gives a value of T_i = 273 ± 11°C. Upon heating a sample to 273°C in the same acetone/water solvent and immediately cooling it, a slight increase in mass of 4% was observed. This indicates that some solvent had migrated into the composite, although if the degradation reaction had begun, it was very slow under these conditions. This value for T_i can be used to calculate T_{Av} which is necessary to determine a value for $k_{R,H}$ at any process temperature as demonstrated in Section 3.4.3.

3.4.2 Shrinking Core Model

In addition to fitting the data obtained to Arrhenius-type equations, a kinetic model can be developed through the application of an SCM. This assumes that the reaction first occurs at the particle surface and, as time

progresses, the reactants move into the particle leaving behind a product or "ash" layer. Therefore, there is an unreacted core which gradually shrinks over time until it disappears. This process is illustrated by **Error! Reference source not found.** and described in detail by Levenspiel, et al [27]. By considering various geometries and rate determining steps, a range of rate equations can be developed to describe the reaction. The only one which fitted the experimental data was that for a reaction rate limited spherical particle. Studying the XRCT image in **Error! Reference source not found.**b, it does appear that there is an approximately spherical volume of resin remaining in the centre of the composite which is gradually degraded over time. This rate equation is expressed by Equation (18) [27] which has previously been selected to model the decomposition of an epoxy resin [11]. As previously stated, the degradation of the composite material starts at some temperature below 300°C, therefore, it is necessary to consider a heating time, t_H (min) in addition to the reaction time, t_R. This is included in the SCM as shown by Equation (19). As this is in a linear form, a plot of $1-(1-X)^{\frac{1}{3}}$ vs. $(t_H + t_R)$ will give a straight line with a gradient equivalent to the rate constant, k_{SCM} (min^{-3}). Values for k_{SCM} are provided in Table 7. This rate constant will also change with temperature and is therefore an average of the heating and reaction phases. However, it is dominated by the reaction time as **Error! Reference source not found.** illustrates that RD is less than 25% for all temperatures except 360°C.

$$1-(1-RD)^{\frac{1}{3}} = kt \tag{18}$$

$$1-(1-RD)^{\frac{1}{3}} = k_{SCM}(t_H + t_R) \tag{19}$$

Temperature (°C)	k_{SCM} (x10^{-3} min^{-3})	R^2
300	1.23	0.98
310	2.49	0.99
320	4.33	0.99
330	8.02	0.96
340	15.8	0.98
360	49.7	0.99

Table 7. Rate constants for the SCM at all temperatures investigated.

Equation (19) can be rearranged to give Equation (20) which can then be used to predict RD at the temperatures investigated. The model, given by the continuous lines in **Error! Reference source not found.**, generally shows good agreement with the data points although it does slightly underestimate the resin decomposition at 300°C. This is further evaluated in Section 3.4.3.

$$RD = 1 - \left(1 - k_{SCM}(t_H + t_R)\right)^3 \quad (20)$$

3.4.3 Model Evaluation

In order to assess how well the models fit the data, each residual was plotted against the observed value of RD. **Error! Reference source not found.** illustrates that the points are randomly scattered around the horizontal axis; the lack of a clearly defined curve is indicative that the regression lines fit the data well, standard deviation is constant across the data set and there is not a systematic error present. The average absolute values of the residuals and standard deviations for each temperature are presented in Table 8 and there is little difference between the two kinetic equations applied. For the Arrhenius model, 53% of the residuals are positive which is similar to the 50% expected if any deviation between the model and experimental data is due to random error. However, 60% of the residuals are positive for the SCM demonstrating a slight tendency to underestimate the RD. This is possibly due to the use of an average rate constant (k_{SCM}) over the whole temperature range investigated and, as there is some degradation during the heating phase, it is possible that the model does not effectively account for this. However, the majority of the data points (82% for the Arrhenius model and 73% for the SCM) lie within ±5% of the measured value for RD. This suggests that both models are able to predict the decomposition to a reasonable degree of accuracy at the temperatures investigated.

Temperature (°C)	Arrhenius Model		Shrinking Core Model	
	Average Residual	Standard Deviation	Average Residual	Standard Deviation
300	2.2%	1.8%	4.0%	2.0%

310	1.8%	1.6%	2.4%	1.7%
320	5.3%	3.7%	1.9%	2.5%
330	3.9%	5.0%	5.3%	5.8%
340	2.7%	3.5%	2.2%	2.8%
360	2.3%	3.9%	0.5%	0.6%
Average	3.0%	3.3%	2.7%	2.6%

Table 8. Values for average residuals and standard deviation across each temperature investigated.

To estimate RD at different temperatures, an Arrhenius plot was drawn (**Error! Reference source not found.**) using the calculated values of $k_{A,R}$ and k_{SCM}. From this, the frequency factor, k_0, and activation energy, E_A, were determined from the intercept with the y-axis and the gradient of the trend line respectively. These values are provided in Table 9. E_A calculated using the Arrhenius model is approximately double that from earlier studies [10] while E_A determined from the SCM is 40% higher [11]. The observed differences are likely attributable to different polymers and solvent systems. The Arrhenius expression (Equation (21)) allows a rate constant for both models at any temperature to be determined. k_H was calculated through rearranging Equation (16) to give Equation (22) and a value of T_{av} was found from Equation (17) assuming that T_i = 273°C.

$$k = k_0 e^{-\frac{E_A}{RT}} \tag{21}$$

$$k_H = \frac{k_R}{e^{-\frac{E_A}{R}\left(\frac{1}{T_R}-\frac{1}{T_{Av}}\right)}} \tag{22}$$

Model	Frequency factor, k_0 (min^{-1})	Activation energy, E_A ($kJ.mol^{-1}$)
Arrhenius	7.64 x10^{17} min	222.3
Shrinking Core Model	1.29 x10^{12} min	164.3

Table 9. Arrhenius kinetic parameters for the SCM and Arrhenius models.

In order to test the models, additional experiments were conducted at 315, 325, 335 and 345°C. These gave values for RD in the range 36.3 to 96.4%; Figure 13 presents the experimental data and predictions using both the Arrhenius and SCM approaches. At lower temperatures, both models underestimate the RD, however, it is apparent that the Arrhenius model gives a value closer to the observed result in all experiments. Upon increasing the reaction temperature, and hence the decomposition of the resin, the models begin to slightly overestimate RD. As t_R increases, both models will tend towards 100%, however the experimental data plateaus at 91 and 95% at 320 and 330°C respectively. This is possibly due to the presence of high molecular weight compounds which require higher temperatures to completely degrade. This would decrease the observed value for RD, although the resin has largely been broken down into monomeric compounds. Despite these observed differences, both models predict a value for RD within 5% of the measured result which is the same as the majority of the data points shown in **Error! Reference source not found.** and 10. It therefore appears that Equation (21) is able to effectively determine suitable values of rate constants in both the developed Arrhenius and shrinking core models. Of the two approaches taken, the application of a series of Arrhenius-type equations appears to be slightly more accurate than the SCM, however, there is additional complexity due to the need to calculate a value for $k_{A,H}$.

4 Conclusion

In this work, the degradation of a CFRP consisting of a thermoset epoxy resin (RTM6 matrix), has been investigated in order to identify the minimum necessary operating conditions when using an acetone/water solvent mixture supplied in the ratio of 80:20 v/v. Temperatures in the range of 300 to 380°C, pressures from 15.8 to 30.0 MPa and reaction times up to 150 min have been studied. Through the application of PC-SAFT, it is also apparent that this solvent system is supercritical for all conditions investigated.

Clean fibres can be recovered using temperatures above 320°C and, as expected, raising the temperature results in significantly faster reaction rates. At 340 and 360°C, the resin was completely decomposed in just 45 and 15 minutes respectively. However, at more extreme conditions, there is significant damage to the fibres as they lose their weave architecture and exhibit a “fluffy” texture. This is likely to severely limit any future applications, therefore, it is desirable to minimise the reaction temperature. For this reason, conditions in the range of 320 to 330°C (19.7 to 22.0 MPa) are recommended. At this temperature, it is possible to recover clean fibres in a reasonable reaction time of 90 to 120 min. Furthermore, this work demonstrates that

the overall process efficiency can be improved through increasing the reactor loading. Even at the highest concentration of 90 g L^{-1}, the degradation still appears to be reaction rate limited and is not controlled by any of the mass transfer stages. This may have important industrial applications when considering the scale-up of the process.

Two different kinetic models were also fitted to the experimental data and were used to predict the resin decomposition at a range of temperatures, with the results showing that either Arrhenius-type equations or an SCM are appropriate. Although slightly more accurate, the application of the Arrhenius equation is more complex. As the use of alternative solvent systems for the decomposition of other resins is further investigated, this additional complexity may need to be taken into consideration.

Nomenclature

Symbol	Definition
$\hat{a}^{assoc}$	Helmholtz free energy due to associative bonding (J mol^{-1})
$\hat{a}^{dis}$	Helmholtz free energy due to dispersive interaction(J mol^{-1})
$\hat{a}^{hc}$	Helmholtz free energy due to hard chain fluid formation (J mol^{-1})
$\hat{a}^{res}$	Total residual Helmholtz free energy (J mol^{-1})
CFRP	Carbon fibre reinforced polymer
DSC	Differential scanning calorimetry
E_A	Activation energy (kJ mol^{-1})
EoS	Equation of state
GRAS	Generally recognised as safe
HTP	High temperature & pressure
k	Boltzmann constant (J K^{-1})
k0	Frequency factor (min^{-1})
$k_{A,H}$	Arrhenius rate constant for the heating phase (min^{-1})
$k_{A,R}$	Arrhenius rate constant for reaction phase (min^{-1})
k_{ij}	Binary interaction parameter (dimensionless)
kSCM	Rate constant for shrinking core model (min^{-1})
LTP	Low temperature & pressure
m	Segment number for PC-SAFT EoS
M	Mass fraction of resin remaining in composite

$m_{composite}$	Mass of composite (g)
m_f	Final mass of sample after calcination (g)
M_H	Mass fraction of resin remaining in composite after heating phase
m_i	Initial mass of the composite (g)
m_p	Mass of resin in the composite after processing (g)
m_{resin}	mass of resin (g)
M_T	Total mass fraction of resin remaining after processing
n	Order of reaction
PC-SAFT	Perturbed Chain - Statistical Associating Fluid Theory
R	Ideal Gas Constant (J mol^{-1} K^{-1})
$-r_A$	Reaction rate (min^{-1})
RD	Resin decomposition (wt.%)
R_i	Initial resin content (g)
R_p	Resin content after processing (wt.%)
RTM	Resin transfer moulded
SCM	Shrinking core model
T	Temperature (°C)
T_{av}	Average temperature between T_i and T_R (°C)
T_g	Glass transition temperature (°C)
TGA	Thermogravimetric analysis
t_H	Heating time (min)
T_i	Initiation temperature (°C)
t_R	Reaction time (min)
T_R	Reaction temperature (°C)
vCF	Virgin carbon fibre
XRCT	X-Ray Computer Tomography
ε/k	Segment energy (K)
κ^{AB}	Association volume of PC-SAFT
σ	Segment diameter (Å)

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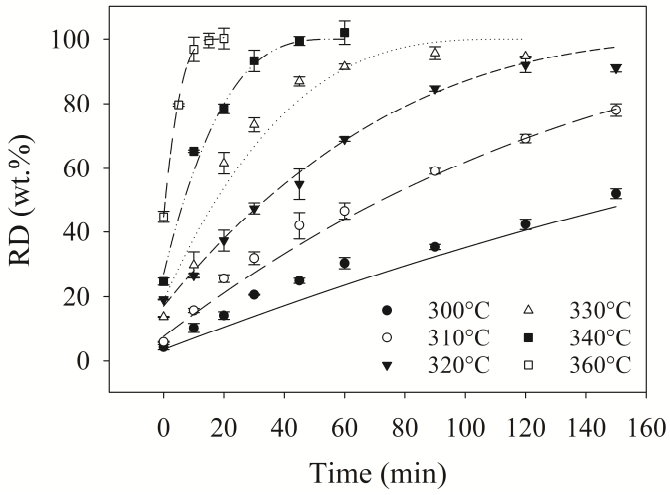

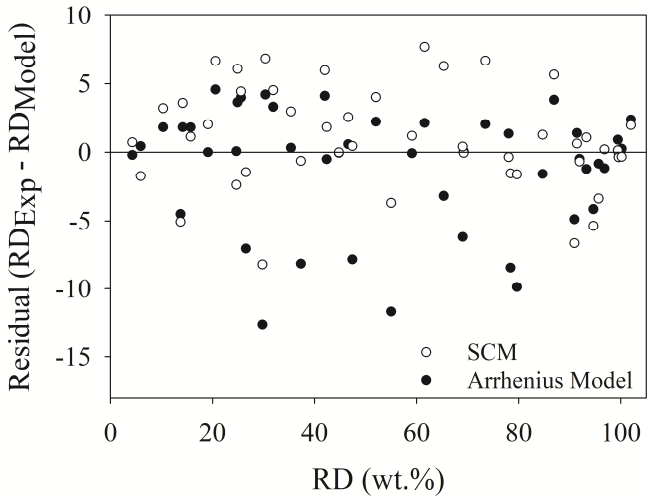

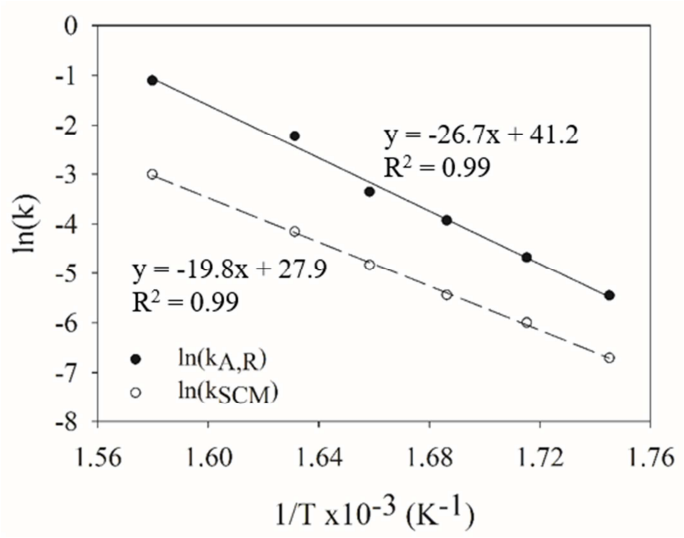

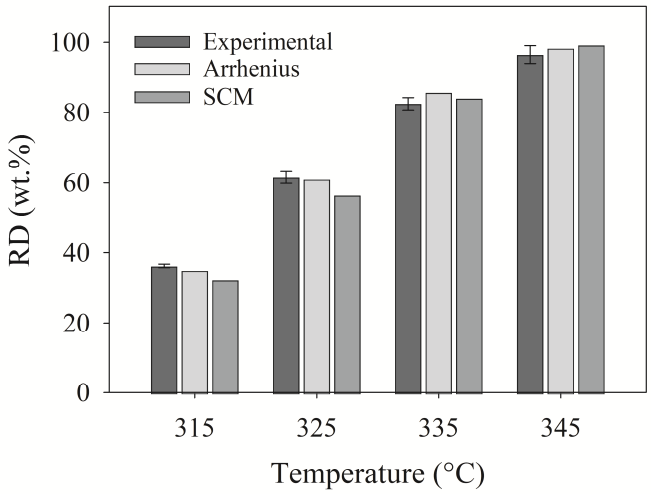

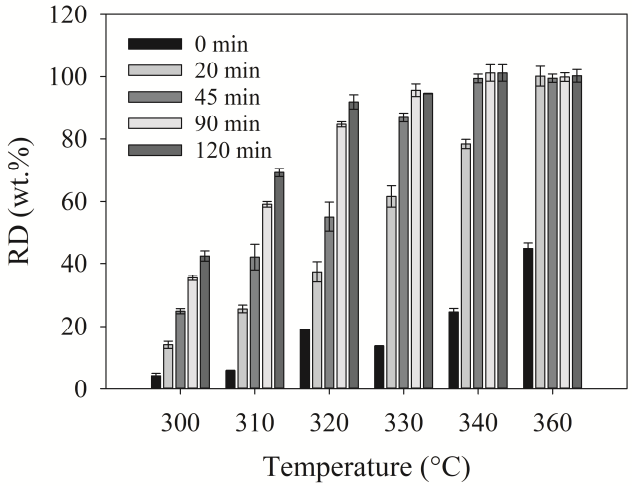

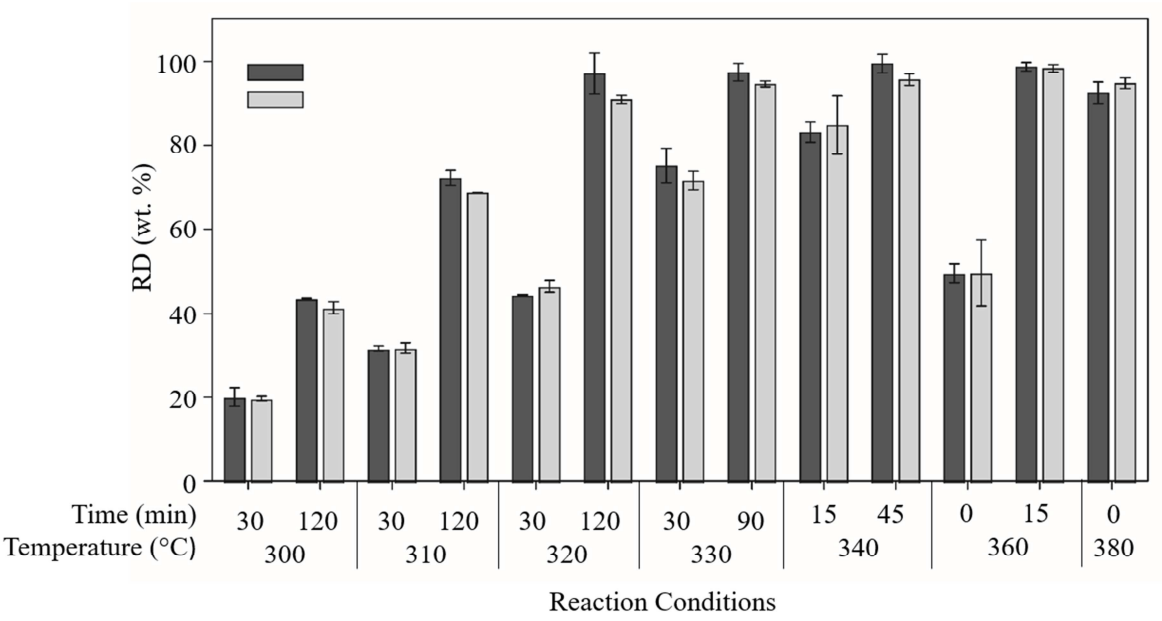

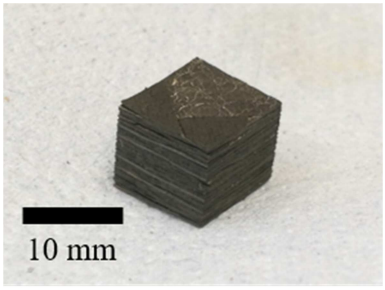

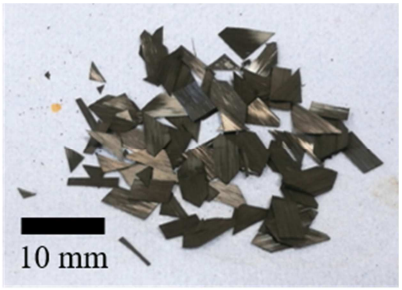

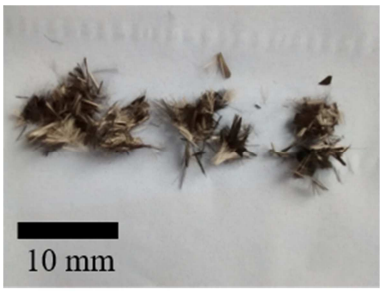

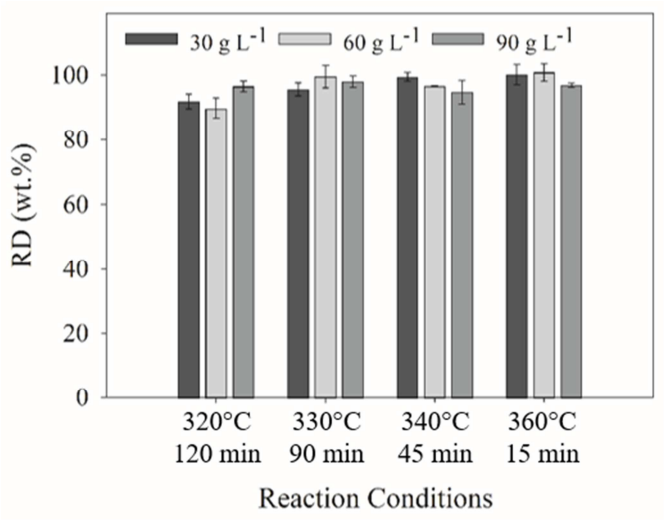

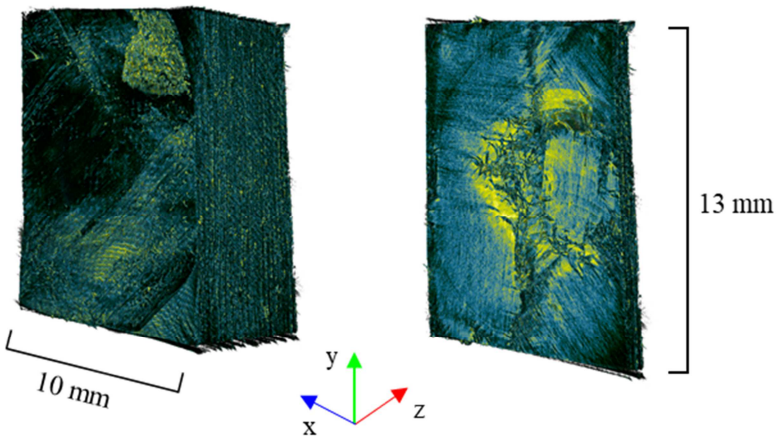

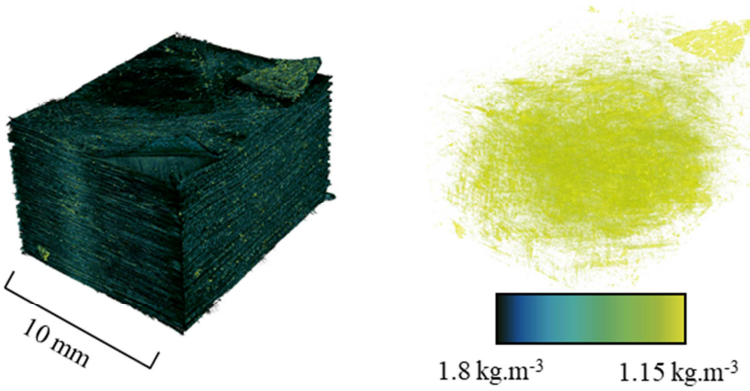

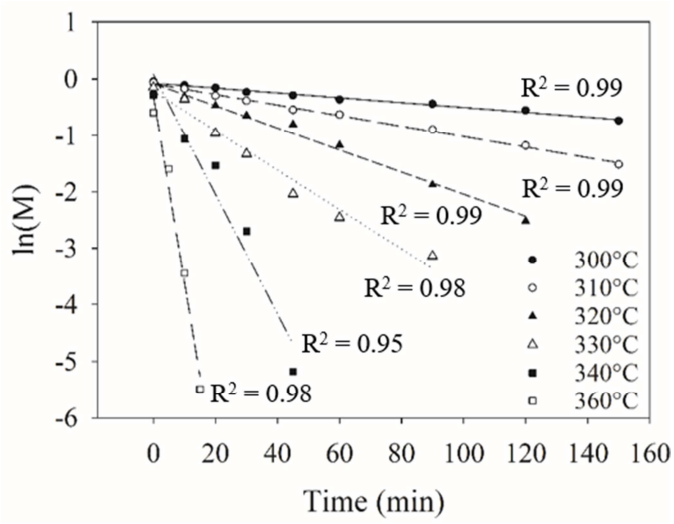

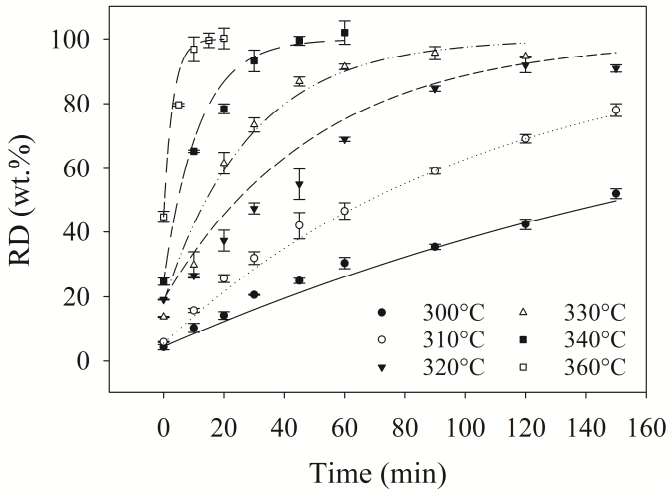

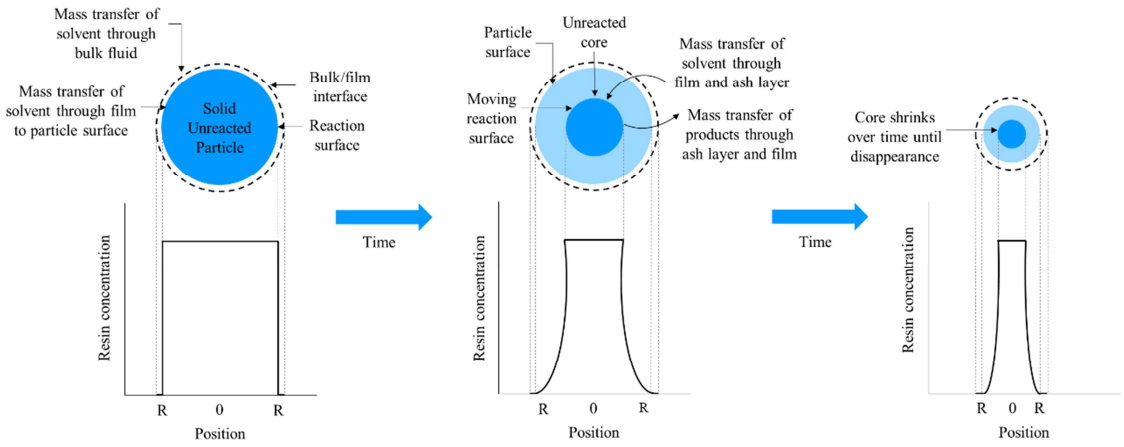

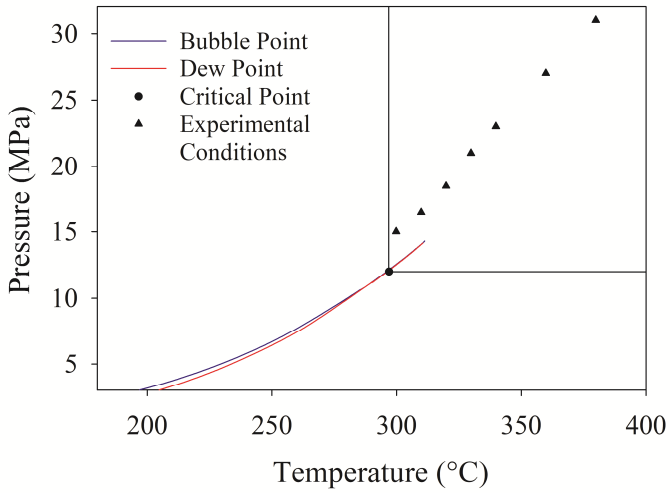

Highlights

for

Recycling a Carbon Fibre Reinforced Polymer with a Supercritical Acetone/Water Solvent Mixture: Comprehensive Analysis of Reaction Kinetics

Matthew J. Keith, Luis A. Román-Ramírez, Gary Leeke, Andrew Ingram

- The degradation of a composite material using an acetone/water mixture was studied.
- To recover clean fibres, a minimum temperature of 320°C for 120 min is necessary.
- Increasing the reactor loading from 30 to 90 g/L does not affect the degradation.
- Shrinking core and Arrhenius-type models were fitted to the experimental data.
- E_A is 164 to 222 kJ/mol and both models can predict the degradation to within ±5%.